Guido Canzona

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METHOD AND COMPOSITION FOR METAL FREE FORM FABRICATION

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Field of the Invention

The present invention relates to metal free form fabrication,
10   and more particularly to the formation of a green part by layered-
build powder processes, such as selective laser sintering and
subjecting the green part to a thermal cycle to form a finished part
having a relatively high density.

15   ## Background Art

Metal free form fabrication by layered-build powder
processes such as selective laser sintering (SLS) can be utilized to
fabricate parts which have a configuration which would make the
parts difficult or impossible to achieve by many prior art processes.
20   The formulation which is used in this process is a powdered blend
of a parent alloy, a lower-melting-temperature alloy, and polymer
particles. The lower-melting-temperature alloy may have
substantially the same ingredients as the parent alloy, with the
addition of a minor amount of a eutectic forming element in the
25   lower-melting-temperature alloy. A thermoplastic polymer, such as
nylon, functions to bind the particles of two alloys during the
selective laser sintering, and upon heating leaving a thin coating of

carbon on the metal powder particles when it is burned away. The carbon remaining from the polymer serves as a residual binder and sintering aid, further reducing the melting temperature of the particles. A thermosetting polymeric binder, such as bismaliimide

5   (BMI) is also added to retain sufficient binding above the remelting temperature of the thermoplastic binder to avoid any crumbling or collapse of the green part while raising the green part temperature in to the range where metal sintering starts to provide green part strength.

10   After the "green" part is formed by selective laser sintering, the green part is then placed into a furnace and subjected to a continuous thermal cycle which sequentially removed the bulk of the SLS binder and the BMI binder then densified the green part with supersolidus liquid phase sintering (SLPS) to form the final

15   product, which is a higher density metal part having the desired end configuration. This prior art process is disclosed in three U.S. patents, namely, U.S. 5,745,834 (Bampton et al) U.S. 5, 932,055 (Newell et al) and U.S. 6,365,093 (Ryang et al). The present invention is directed toward the optimization of the basic prior art

20   method.

Brief Description of the Drawings

Fig. 1 is a graph which appears in Fig. 3 of U.S. 5,932,055 and represents a prior art continuous thermal cycle, which is described in U.S. 5,932,055;

5 Fig. 2 is a graph which shows somewhat schematically the effect of powder size of the parent alloy and the lower-melting-temperature alloy relative to affecting sinterability;

Fig. 3 is a table representing a comparison of a first powder blend and the powder blend of an embodiment of the present

10 invention;

Fig. 4 illustrates the microstructure and density of specimens sintered in accordance with the embodiments of the present invention;

Fig. 5 is a graph with illustrations plotting density of the end

15 product that is formed by utilizing the embodiment of the present invention, in comparison with sintering temperature ranges outside the scope of the range specified in the embodiment of the present invention;

Fig. 6 is a table showing the processing conditions during the

20 thermal cycle of the embodiment of the present invention.

Fig. 7 is a graph illustrating the performance obtained by the embodiment of the present invention in comparison with other metal forming processes.

Description of the Preferred Embodiments

This embodiment of the present invention relates to metal free form fabrication and more specifically to accomplishing the free form fabrication using a layered-build powder process, such as selective laser sintering (SLS), of a blend of metallic and polymer particles to form a green body, followed by thermal consolidation of the green body into a solid metal part. A basic method that presently exists in the prior art is disclosed in three U.S. patents, namely U.S. 5,745,834 (Bampton et al), U.S. 5,932,055 (Newell et al) and U.S. 6,365,093 (Ryang et al).

This embodiment of the present invention is directed toward making improvements in this technology relating to the formulation of the blend itself, and also relating the methods disclosed in those patents. Accordingly, it is believed that a clearer understanding of the present invention can be obtained by first describing the formulation and methods of the prior art as presented in these three prior art patents (U.S. 5,745,834, U.S. 5,932,055 and U.S. 6,365,093) and then describing the improvements provided by this embodiment of the present invention.

In describing the prior art as presented in these three patents, there will first be an overall description of the formulation and the methods disclosed in those patents with a focus more on those areas where improvements have been made by this embodiment of the present invention. Obviously, for the sake of brevity, every item of information in these three prior art patents is

not contained in this text of the present patent application. However, the subject matter of these three prior art patents are hereby incorporated by reference in the present patent application so that if at a later time it would be appropriate for providing a

5   proper disclosure of the subject mater of this present application to incorporate information from these three patents, this would be done with the understanding that the applicant reserves the right to incorporate such disclosures into the present patent application by amendment, so that this would not be deemed to be incorporating

10   new matter.

The formulation of the metal/polymer powder blend, as disclosed in those three prior art patents, is a blend of four powders, namely,

a)   a parent metal alloy,

15   b)   a lower-melting-temperature alloy,

c)   a thermoplastic organic polymer,

d)   a thermosetting organic polymer

The lower-melting-temperature alloy is made by introducing a minor amount of a eutectic forming element into the alloy. A

20   thermoplastic polymer, such as a nylon, functions to bind the metal powder particles during the layered-build process and a thermosetting polymer, such as a bismaliimide, acts to continue binding the metal powder particles after the thermoplastic binder remelts and is baked off in a furnace debind and densification

25   process. The thermosetting polymer is backed off at a higher temperature after metal particle sintering has initiated sufficiently to provide green part strength and stiffness. Carbon residue from the

two organic binders, serves as a residual binder and sintering aid, and also further reducing the melting temperature of the metal particles.

The first step is to mix the powders of the four main components, namely the parent or base metal alloy, the lower-melting-temperature alloy, and the two polymer binders. In U.S. 5,932,055, the parent metal alloy is a nickel based super 230 alloy which comprises about 75-85% by volume of the total blend, and which contains only a trace (or none) of boron. The lower-melting-temperature alloy is a borided 230 alloy which constitutes about 5-15% of the volume, with this borided 230 alloy being 3.4% to 3.9% boron by weight. As disclosed in U.S. 5,932,055 the remainder is the organic polymers. The average particle size of polymer binders is 5 microns., and is 5-15% of total volume. This formulation of the prior art blend, as disclosed in U.S. 5,932,055, will be disclosed more completely later in this patent application.

Then the technique of layered-build powder processing, such as, selective laser sintering (SLS) of the powder blend is utilized to form the green body. This is accomplished by utilizing a machine to lay down successive thin layers of the powder blend and utilizing the laser to selectively melt the binder in each layer prior to the laying down of the next layer, in accordance with the three dimensional design of the finished part. This can be accomplished in accordance with a three dimensional computer aided design (3D CAD) method where the data is supplied by a computer. As each layer of the blend is laid down and treated by the SLS technique the three dimensional green body is formed.

Then the green body that is formed is taken out of the SLS machine, and the excess powder is brushed off or otherwise removed, and the green body is transferred to a vacuum furnace to be de-binded and densified. During this time, the green form part

5   may be supported in some manner, such as being positioned in ceramic boats, or if there are complex parts being packed in boron nitride powder inside a ceramic crucible or by addition of connected or un-connected features to the green body that will be removed from thefinal densified part. As disclosed in the prior art,

10   this green form part typically would have a relative density of approximately 55%.

The vacuum furnace in which the green form part is placed is desirably computer controlled in a manner that the temperature and furnace atmosphere are precisely adjusted. In the prior art,

15   the green form part may be subjected to a single continuous thermal cycle. Such a cycle is illustrated in a graph which appears as Fig. 3 of U.S. 5,932,055, and this same graph of U.S. 5,932,055 is shown in the drawings of this patent application as Fig. 1 and is designated as "prior art".

20   As can be seen in Fig. 1, the temperature in the furnace is initially brought to a temperature between 200°C and 500 °C so that the thermoplastic polymer is baked off to leave a deposit of residual carbon throughout the blend. Volatilization occurs in the early stages of heating causing a breakdown of the polymer as

25   hydrogen, nitrogen, and oxygen, and some of the carbon is off-gassed from the part. The remainder of the volatile carbon reacts with metal oxides in the surface of the particles to form a thin

carbon film whose C=C bonds maintain the shaped part. The rate of reduction should be controlled such that the pressure in the furnace to accomplish the out-gassing is always less then the bond strength of the particles to avoid exploding the green formed part.

5   Then, the furnace temperature is increased from about 500°C to about 1200°C.

As disclosed inU.S.6,365,093, the thermosetting polymer binder hardens prior to remelting of the thermoplastic binder and thereby provides critical support of the green body shape while

10   heating up to the temperature where metal-to-metal powder sintering (neck formation at points of powder contact) initiates to provide increasing green body strength.

Once necessary thermal conditions are achieved and the boron content has reached equilibrium, the supersolidus liquid

15   phase sintering (SLPS) begins, and this is accomplished in U.S. 5,932,055 in a temperature range from about 1200-1300°. A liquid forms along the grain boundaries and the particles neck down due to the elevated levels of the eutectic reducing element. This liquid phase promotes grain boundary sliding of the polycrystalline

20   particles.

The various effects that occur during this period of supersolidus liquid phase sintering (SLPS) is described more completely in U.S. 5,932,055 beginning on column 7, four lines from the bottom, and continuing on through column 8 beginning at

25   the top of column 8 and continuing on through line 48.

During this treatment in the furnace, the green part densifies (decreases in volume) and as the temperature in the oven

decreases, the liquid content in the part solidifies in the form of a finished part. It is desirable that the surface on which the green part is positioned has a sufficiently low coefficient of friction so that the reduction of size of the green part is not impeded by

5 surface friction during shrinkage and densification.

With regard to the materials which form the blend, as described in U.S. 5,932,055, the elements which comprise the 230 alloy that is the parent alloy given as follows:

Element	Weight Percent
Ni	Balance
Cr	22
W	14
Mo	2
Fe	3
Co	5
Mn	0.5
Si	0.4
Al	0.3
C	0.1
La	0.02
B	0.005

The following three paragraphs are quoted directly from U.S. 5,932,055, but with some minor changes to delete some numerical

25 designations and some minor clarifications.

"The nickel based Haynes 230 powder was selected for its superior ductile properties but other parent metals such as iron,

cobalt, copper, tungsten, molybdenum, rhenium, titanium, and aluminum, for example, may also be used.

"The eutectic forming element by definition reduces the melting temperature of the parent alloy. The reducing element

5   must also be very small and highly reactive with carbon so that it may become diffusely mobile along the grain boundaries between the individual grains in a Haynes 230 particle. Boron is an intermetallic forming element that reduces the melting temperature of this alloy, is very small and thus highly mobile, and reacts with

10   carbon to form very strong organo-metallic bonds, e.g. B_4 C or B_{12} C_3, that have a melting temperature far above any temperature in the DMF process. Scandium is yet another example. Other metallic elements such as manganese, yttrium, niobium, silicon and cobalt are eutectic but may not have the required diffusion

15   properties.

"The carbon precursor must be capable of wetting and bonding the parent metal alloy in its green form and, when heated, of undergoing a reduction that eliminates the molecules of gaseous elements (hydrogen, nitrogen and oxygen) and leaves a

20   thin carbon film that maintains the structural integrity of the green form part. Typical carbon precursors are organic polymers (P) such as powders or resins or catalytic chemical vapors. Although many organic polymers can be used to produce the carbon film for DMF, only three have real commercial potential as a fine powder:

25   polyester (rayon), polyacrylonitrile (acrylic), and polyamide (nylon). In the preferred embodiment, the carbon is introduced via a fine mesh Nylon-12 high molecular weight polymer powder."

It is to be understood that the information in this text which has been presented up to this point as background information concerning and relating to the three U.S. patents (U.S. 5,932,055, U.S. 5,745,834 and U.S. 6,365,093) already exists in the prior art.

5 With that information having been presented, there will now be description of the features which are combined with these various prior art teachings to make up the embodiments of the present invention.

A goal in arriving at this embodiment of the present invention

10 has been (and is) to accomplish the direct metal fabrication (DMF) of the finished part using the basic processes as described above, but to achieve an improved end product and also obtain greater reliability in the manufacture/fabrication of the product. There have been several discoveries and findings which have been made.

15 One of the findings is that in order to achieve higher density, it would be necessary to achieve a higher metal density in the SLS green part. More specifically, the goal has been to reach a sinter densification at least as great as 96% of full density or greater, and to achieve this the metal density of the SLS green part should be

20 at least as great as about 58% relative density or greater. It was discovered that densification by more than a 38 percentage point increment (eg., 58% density to 96% density) was the maximum achievable in practice by the liquid phase sintering whilst maintaing control of part final shape and dimensions.

25 In accomplishing this, it was also found that the metal powder size distribution needs to be optimized to provide sufficiently high packing density for subsequent sintering to the

required high density (96% or greater). Further, in accomplishing this, it was found that there should be a different balance in the percentage amounts of the three binders (i.e. the thermoplastic, the thermoset and the boron) to obtain the required sinter

5 densification. More specifically, to accomplish 96% density or greater, the percentage amount of polymer used is reduced and the percentage amount of the borided metal powder (low-melting-temperature component of the powder blend) relative to the percentage of polymer was increased relative to previously

10 practiced methods.

In developing the method of this embodiment, there was provided a dedicated metal powder sintering furnace to allow very close control of temperature cycles, temper distributions throughout the furnace and changeable gaseous/vacuum

15 . environments within the furnace in a continuous automated cycle which does not require moving the part until the entire thermal process cycle is complete.

This furnace is a commercial furnace which already exists in the prior art and the containing structure of the furnace comprises

20 an inside "box" and an outside "box", and in the area between the two boxes there are heating elements throughout the area between the two boxes. The circulation of the gas (primarily an inert gas such as argon) in the chamber of the furnace is done through the side walls of the inner box where there are a large

25 number of orifices spread around the inside box. There are two larger exhaust passageways at the bottom portion of the containing structure.

Also, the size of the particles of the alloys (i.e. the parent metal alloy and the lower-melting-temperature alloy) was investigated and there was discovered the need to properly balance the desired high flowability in the SLS machine provided

5   by the larger powder sizes against the well known sintering benefits of the finer particles. The results are illustrated in Fig. 2 which graphically illustrates the effective powder size on the SLS and furnace sinterability.

It can be seen from Fig. 2 that as the mesh size (i.e. from left

10   to right) the relative furnace sinterability improves, (with an increase in mesh number meaning smaller particle size). The larger particle size favors SLS sintering. As a balance, sizing the powder so that a predominant percentage of the particles pass through a 325 mesh screen (U.S. mesh), a proper balance was

15   achieved. Thus 325 mesh screen will pass particles of 0.00176 inch or smaller, and there would be a normalized distribution of the larger and smaller particles. Within the broader scope the mesh screen size could possibly be 270 mesh size, or even as low as 140 mesh size, or at a greater mesh size such as 400 mesh size.

20   With regard to the amount of the lower-melting-temperature alloy (which in this embodiment is a borided alloy), the amount of borided alloy is this embodiment about 15% of the total weight of the blend of three components (i.e. the parent metal alloy, the lower-melting-temperature alloy and the organic polymer). This

25   could be possibly as high as 17%, 16%, 18% or 20%, or possibly higher or as low as 14%, 13%, or 12% or lower, but beyond those

limits present analysis indicates that this would be a non-optimized balance.

The amount of organic polymer particles, is by weight in embodiment less than 3% of the total weight of the blend of the three components, and in the embodiment disclosed herein 0.5%. It is less effective to go much below that, but it possibly could go as low as 0.4% or even possibly 0.3% in certain circumstances. However, in general this would decrease the ability of the organic molecular component to bind the particles together during the SLS (selective laser sintering) operation. This amount could go higher to, for example, 0.6%, 0.8%, or 1.0%, or possibly higher to 1.2%, 1.5%or 2.0%, but moving in that direction in general decreases the density of the SLS green part and as a result the density of the end product. However, in some situations the higher levels of the organic polymer could possibly be used with the sacrifice of the density, where the requirements for the finished part are less critical.

Thus, the ratio of the lower-melting-temperature alloy to the organic polymer by weight in the blend of the three components is at least as great as 5:1, and can be at least as great as 10:1, 15:1, 20:1, 25:1, 30:1 or possibly up to 35:1 or higher.

In Fig. 3, there is shown a table showing the various characteristics of the three components of the blend. In the upper row, there are given the characteristics of the blend in accordance with what the applicants' investigation indicates what is thought to be an optimized quantity in the prior art, this being identified as "original". In the second row, there are given the values which are

present in this one example of the embodiment of this embodiment of the invention. It can be seen that in the prior art, the size of the metal particles in the prior art was for 55% 88 to 44 micron size, and 45% is at the 44 micron size. On the other hand, in the new

5　formulation, 100% of the particles in the metal powder category are 44 microns or less.

With regard to the non-borided parent metal alloy, the percent of the total amount in the prior art is 90%, while in the

10　present embodiment, it is down to 85%.

With regard to the borided alloy, the weight percentage of the total in the prior art is 10% and in the embodiment of the present invention it is 15%. At the very right of Fig. 2, there is given the percentage of boron in the borided alloy and this remains at 0.5%

15　for both the prior and the embodiment of the present invention.

With regard to the percentage of nylon by weight, this dropped from 3% to 0.5% from the prior art amount to that of this embodiment of the present invention.

Another discovery which was made during the course of

20　developing this embodiment of the invention is that when the formulation parameters described previously in this text were followed, in order to achieve optimum density the processing temperature is maintained during the supersolidus liquid phase sintering (SLPS) should be maintained within a narrow range. This

25　range is between approximately 2250°F (1332°C) and 2260°F (1237°C), with a middle figure being 2255°F (1235°C). To demonstrate this, sintering trials were conducted at temperatures

ranging from 2248°F (1231°C) to 2267°F (1241°C). Figure 4 illustrates the effect of the sintering temperature of 2255°F on the density and micro structure of DMF alloy 230. A favorable micro structure and density resulted only from specimens sintered within

5 the narrow but achievable temperature range of 2252°F (1233°C) to 2260°F (1237°C). This is shown in the graph of Fig. 5.

It was further discovered that if this sintering temperature during the SLPS stage is too low the consolidation is insufficient. On the other hand, if it goes above a higher temperature limit, then

10 the metal boride phase that forms on solidification of the liquid phase takes the form of large primary particles which embrittle the final material. An optimum temperature range exists for adequate sinter densification without slumping and provision of a microstructure that has a desirable combination of strength,

15 ductility, toughness and fatigue resistance for structural engineering applications.

To describe the thermal cycle of this embodiment of the present invention, reference is made to Fig. 6. It can be seen that in the powdered blend that was used to make the green part, the

20 polymer (N-12) is 0.5%, and the percent of boron in the low melting temperature alloy was 0.5%.

During the debind cycle the rate at which the temperature was raised in the chamber of the furnace was 2°F per minute, and this rate of increase was maintained until the temperature rose to a

25 temperature of 1652°F (900°C). The hold time at that temperature was 15 minutes; the pressure was 700 torr, and the gas in the chamber was argon.

Then to start the sinter cycle, using the sinter cycle, the temperature was raised from 1652°F (900°C) at a rate of 1°F per minute up to a holding temperature of 2255°F (1235°C). The hold time at this temperature was ten minutes, and the pressure was

5   300 torr the gas that was injected into the oven was 95% argon, and 5% hydrogen, measured by volume at the same temperature and pressure.

The reason for combining hydrogen gas with the argon is two-fold. Firstly the argon is a relatively poor conductor of heat,

10   while, on the other hand, hydrogen functions as a very good conductor and is able to cause the gaseous mixture in the furnace to be maintained at a precise temperature level. Secondly, the hydrogen content very effectively removes residual oxygen from the furnace atmosphere thereby enhancing liquid phase sintering

15   due to the absence of metal oxide coatings on the metal powder particles. The 5% hydrogen level, could be raised, but this could raise other problems, for example, relating to hydrogen being an inflammable gas.

The hold time at the 2255°F temperature is ten minutes or

20   less and after that the temperature in the chamber of the furnace is lowered to a level closer to ambient temperature.

To demonstrate the results achieved by this embodiment of the invention, reference is made to Fig. 7. Tensile testing was performed to confirm the sintering profile provided by material

25   properties comparable to investment cast and wrought 230 alloy. Approximately twenty five green body round bars in the three primary build directions, X, Y, and Z were sintered, HIP'ed and

machined into tensile specimens. Tensile tests were performed at room temperature and at 1000°F. Fig. 7 contains the average of all DMF 230 alloys tensile results compared to wrought and cast properties. Except for ductility, DMF 230 alloy exceeds cast

5   material strengths and is comparable to wrought strengths. Although lower in ductibility, for many applications, the resulting DMF elongation is more than sufficient for use.

It is to be understood that various modifications could be made to the embodiment without departing from the teachings of

10   the present invention.